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1. Introduction

Given the rising concerns about the energy shortage and environmental pollution, the conversion of renewable biomass to liquid fuels has attracted increasing attention.^{1–5} Lignocellulose, the most abundant biomass, is generally considered to be a sustainable feedstock for energy, chemicals and biofuels.^{6–8} As the second largest component in ligno-

Eco-friendly preparation of ultrathin biomassderived Ni₃S₂-doped carbon nanosheets for selective hydrogenolysis of lignin model compounds in the absence of hydrogen[†]

Changzhou Chen, (¹)^{ta,c} Dichao Wu, ¹)^{ta,c} Peng Liu,^{a,c} Jing Li,^{a,c} Haihong Xia,^{a,c} Minghao Zhou ¹ *^b and Jianchun Jiang*^{a,c}

Lignin is an abundant source of aromatics, and the depolymerization of lignin provides significant potential for producing high-value chemicals. Selective hydrogenolysis of the C-O ether bond in lignin is an important strategy for the production of fuels and chemical feedstocks. In our study, catalytic hydrogenolysis of lignin model compounds (β -O-4, α -O-4 and 4-O-5 model compounds) over Ni₃S₂-CS catalysts was investigated. Hence, an array of 2D carbon nanostructure Ni₃S₂-CSs-X-Y derived catalysts were produced using different compositions at different temperatures (X = 0 mg, 0.2 mg, 0.4 mg, 0.6 mg, and 0.8 mg; Y = 600 °C, 700 °C, 800 °C, and 900 °C) were prepared and applied for hydrogenolysis of lignin model compounds and depolymerization of alkaline lignin. The highest conversion of lignin model compounds (β -O-4 model compound) was up to 100% and the yield of the obtained corresponding ethylbenzene and phenol could achieve 92% and 86%, respectively, over the optimal Ni₃S₂-CSs-0.4-700 catalyst in iPrOH at 260 °C without external H₂. The 2D carbon nanostructure catalysts performed a good dispersion on the surface of the carbon nanosheets, which facilitated the cleavage of the lignin ether bonds. The physicochemical characterization studies were carried out by means of XRD, SEM, TEM, H₂-TPR, NH₃-TPD, Raman and XPS analyses. Based on the optimal reaction conditions (260 °C, 4 h, 2.0 MPa N₂), various model compounds (β -O-4, α -O-4 and 4-O-5 model compounds) could also be effectively hydrotreated to produce the corresponding aromatic products. Furthermore, the optimal Ni₃S₂-CSs-0.4-700 catalyst could be carried out in the next five consecutive cycle experiments with a slight decrease in the transformation of lignin model compounds.

> cellulose, lignin is an attractive renewable source of aromatic building blocks to supply aromatic chemicals.^{9,10} Thus, numerous approaches including hydrogenolysis,¹¹ fast pyrolysis,¹² hydrolysis¹³ and enzymolysis¹⁴ have been employed to generate aromatic products from lignin. In recent years, the cleavage of the β -O-4 ether bond in lignin model compounds is usually investigated as the first step in order to seek novel catalysts for the valorization of lignin as it is the abundant linkage than 4-O-5 and α -O-4 ether bonds and has a lower bond dissociation energy than the C-C bond in lignin.15-18 Indeed, many researchers reported the catalytic cleavage of the β -O-4 ether bond in lignin over different types of catalysts. For example, Jiang et al. discovered a new Ni/TiO₂-photocatalytic route for the cleavage of 2-phenoxy-1-phenylethan-1-ol to obtain acetophenone and phenol through a two-step process.¹⁹ Despite the high efficiency of the cleavage of the β -O-4 ether bond, an excess of oxidant such as pyridinium chlorochromate was needed in the catalytic system that could result in the poisoning of the catalyst and environmental pollution. Thus, the

^aInstitute of Chemical Industry of Forest Products, Chinese Academy of Forestry; Key Lab. of Biomass Energy and Material, Jiangsu Province; National Engineering Lab. for Biomass Chemical Utilization; Key and Open Lab. on Forest Chemical Engineering, SFA, Nanjing 210042, China. E-mail: jiangjc@icifp.cn

^bSchool of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou 225002, China. E-mail: zhouminghao@yzu.edu.cn

^cCo-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, China

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development of a new catalytic system for the cleavage of a β -O-4 ether bond and depolymerization of lignin to obtain aromatic chemicals in an efficient method is still desirable.²⁰

2D carbon nanostructures have shown great potential in vast fields such as catalysis, biotechnology, energy storage and conversion due to the unique electronic properties in the confined dimension of nanophase sp²-hybridized carbon.²¹ Nickel sulfide (NiS), a p-type semiconductor, has also attracted increasing attention due to its low-cost, good electrical properties, and other unique properties such as high photocatalytic effect toward the polysulfide reaction.^{22,23} For example, Li et al. fabricated NiS/CdS nanocomposites using a two-step solvothermal method for hydrogen evolution by photocatalytic reforming of lignin.²⁴ The H₂ evolution rate obtained using the optimized photocatalyst is up to 147.7 μ mol h⁻¹ g⁻¹ ($\lambda \ge 400$ nm) and the apparent quantum efficiency (AQE) was 44.9% from an aqueous solution of lignin. However, NiS/CdS nanocomposites were assembled by a complex two-step solvothermal method. CdS NWs were first synthesized, followed by an impregnation method that was used to prepare CdS NWs that were ultrasonically dispersed in ethylene glycol solution containing nickel nitrate and thiourea. In our work, sodium lignosulfonate was not only used as a carbon source, but also as a sulfur source. It was impregnated with nickel nitrate hexahydrate and boric acid to prepare Ni₃S₂-doped carbon nanosheets in one step. This method made full use of the waste sodium lignosulfonate produced in pulp and papermaking, and the preparation of the catalyst was simpler than many previous research studies, which is fully in line with the concept of green chemistry.²⁵ As far as we know, Ni₃S₂-doped carbon nanosheets are yet to be applied to the hydrogenolysis of biomass, such as lignin model compounds and lignin.

In addition, the employment of H₂ as a hydrogen source in lignin depolymerization will increase the cost of the catalytic reaction and result in unfavorable over-hydrogenation.²⁶ Catalytic transfer hydrogenolysis shows an efficient and green alternative for H₂ in many catalytic reactions, in which hydrogen-donor solvents such as iPrOH, EtOH and MeOH can be easily obtained from renewable resources.²⁷⁻²⁹ Furthermore, the use of hydrogen-donor solvents can reduce security risks and cut the costs associated with the transportation and storage of H₂.³⁰ For example, Luque *et al.* reported the catalytic transfer hydrogenolysis of 2-phenethyl phenyl ether promoted by a bimetallic Pd/Ni system to generate corresponding aromatics.³¹ Hence, the application of catalytic transfer hydrogenolysis in β-O-4 ether bond cleavage and lignin depolymerization has been regarded as a novel alternative to the traditional hydrogenolysis system.

In this study, we first report a facile yet sustainable approach for the production of Ni_3S_2 -doped carbon nanosheets (denoted as Ni_3S_2 -CSs) in one-step with a very thin thickness of 30 nm and excellent flexibility by assembling the biomass molecule in long-range order on a 2D hard template and subsequent annealing. Sodium lignosulfonate was used as a carbon and sulfur source because it was the reaction product of wood pulp with sulfur dichloride and sulfite thus containing a large number of S element.³² Boric acid was employed as a 2D template, which could be readily recycled for repeated use by simple evaporative crystallization from the waste liquid.33 The novel Ni₃S₂-CS catalysts could achieve efficient cleavage of ether bonds including β -O-4, 4-O-5 and α-O-4 under moderate conditions (260 °C, 2.0 MPa N_2 and 4 h). High yields of the corresponding aromatics were obtained (up to 90%) in iPrOH over the optimal catalyst Ni_3S_2 -CSs-0.4-700 (0.4 represented the 0.4 g of $Ni(NO_3)_2$ ·6H₂O and 700 represented the calcination temperature of the catalyst) and the catalytic system also exhibited a broad substrate scope. The physicochemical characterization of all investigated catalysts was performed through XRD, SEM, TEM, H2-TPR, NH₃-TPD, Raman and XPS analyses. The reaction mechanism and intermediate species were extensively discussed in the end.

2. Experimental

2.1 Materials

Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) and boric acid (BH₃O₃) were purchased from Aladdin Industrial Inc. Shanghai, China; sodium lignosulfonate were provided from Sigma-Aldrich; phenyl benzyl ether (>99%), 1-(benzyloxy)-4methoxybenzene (>99%), 1,4-bis(benzyloxy)benzene (>99%), 2-(benzyloxy)phenol (>99%), 3-(benzyloxy)phenol (>99%), 4-(benzyloxy)phenol (>99%), diphenyl ether (>99%), 4,4'-oxybis (methylbenzene) (>99%), 4,4'-oxydiphenol (>99%), 1-methyl-3phenoxybenzene (>99%), anisole (>99%), phenethoxybenzene (>99%), iPrOH (>99%), and n-dodecane (>99%) were obtained from commercial sources and used without further purification. 2-phenoxy-1-phenylethan-1-ol, 2-(2-methoxyphenoxy)-1phenylethan-1-ol and 2-(2,6-dimethoxyphenoxy)-1-phenylethan-1-ol was synthesized according to a literature method.34 N2 (>99.999%) was supplied by a local gas factory. Deionized (DI) water was applied for all experiments.

2.2 General procedure for Ni₃S₂-CSs catalyzed 2-phenoxy-1-phenylethan-1-ol

The typical catalytic reaction was performed in a 25 mL stainless Parr autoclave. 100 mg of 2-phenoxy-1-phenylethan-1-ol or other substrates, 20 mg of Ni_2S_3 -CS catalyst and 10 mL of iPrOH were added to the stainless Parr autoclave and purged with N_2 gas three times in order to exhaust air. The reactions were conducted at 260 °C with 2.0 MPa N_2 and stirred at 600 rpm for 4 h. After the reaction, the reactor was cooled to room temperature and the mixture was filtered to remove the catalyst. Finally, the filtrate was analyzed using a gas chromatograph/mass spectrometer employing *n*-dodecane as an internal standard (GC/MS, Agilent 7890A). The residual catalyst was rinsed with iPrOH and dried to collect for a cyclic test. Yields were defined in total molar basis, and the defined equations for the conversion of 2-phenoxy-1-phenylethan-1-ol and the yields of corresponding products were listed as follows:

$$Conversion = \frac{\text{mole of reacted substrate}}{\text{total mole of substrate feed}} \times 100\% \qquad (1)$$

Yield of phenethoxybenzene

$$= \frac{\text{mole of phenethoxybenzene}}{\text{total mole of substrate feed}} \times 100\%$$
(2)

Yield of ethylbenzene

$$=\frac{\text{mole of ethylbenzene}}{\text{total mole of substrate feed}} \times 100\%$$
(3)

$$\text{Yield of phenol} = \frac{\text{mole of phenol}}{\text{total mole of substrate feed}} \times 100\% \qquad (4)$$

During the reusability tests, the spent catalyst after each run was washed with iPrOH and collected by centrifugation 5 times. Then it was dried overnight in the oven at 100 °C. The experiment was repeated to make up for catalyst loss.

2.3 Catalyst preparation

In a typical run, boric acid (8 g) was dissolved in deionized water at 80 °C, followed by adding sodium lignosulfonate (1 g) under magnetic stirring. The ratio of sodium lignosulfonate and boric acid was fixed at 1:8. It was probably because of the contribution to the thinnest nanosheet structure by the application of 1 g of sodium lignosulfonate and 8 g of boric acid, which was reported in our previous literature.³⁵ Then, nickel nitrate hexahydrate of different quality (0 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g) was added to the mixture. The mixture solution was kept at 80 °C under stirring until the water was evaporated. The dark yellow resultant composite was then annealed at desired

temperatures (600 °C, 700 °C, 800 °C, and 900 °C) for 2 h at a ramp rate of 5 °C min⁻¹ in N₂ flow, yielding a black powdery product. After washing with deionized water three times and ethanol three times. In the end, the obtained black powdery product was dried at 80 °C for 12 h to yield desired Ni₃S₂-CS catalysts. For example, catalysts with 0.4 g of nickel nitrate hexahydrate calcined at 700 °C were denoted as Ni₃S₂-CSs-0.4-700, and other catalysts were also named in this way.

The synthetic strategy of Ni₃S₂-CSs is schematically shown in Scheme 1. Boric acid was dissolved in deionized water at 80 °C, followed by adding the sodium lignosulfonate under magnetic stirring. Then, nickel nitrate hexahydrate of different quality was added to the mixture. The boric acid crystals were first formed by forced crystallization induced by continuous evaporation of its aqueous solution at 80 °C. In this process, sodium lignosulfonate was assembled to the lateral plane of boric acid crystals, inhibiting its layer-by-layer growth and restacking along the *c*-axis by which the boric acid plate got thicker.³⁵ Nickel nitrate hexahydrate was loaded on the surface by impregnation. After annealing at the desired temperature under a N₂ atmosphere, the sodium lignosulfonate layer was converted to carbon nanosheets via thermal-induced polycondensation and carbonization, while boric acid was decomposed into boron oxide (Fig. 1a). The SEM result was similar to our previous study.³⁶ Meanwhile, the S heteroatom and metal Ni were also incorporated into carbon nanosheets upon heating. The boron oxide in the Ni₃S₂-CS precursor could be washed away by ethanol three times and we eventually afforded a pure Ni₃S₂-CS sample after drying in the oven. In the whole process, a large amount of boric acid could be recycled by simply evaporating the waste liquid,³⁶ and could be repeatedly employed as a template material in the next run for



Scheme 1 Schematic illustration of the sustainable synthesis of Ni_3S_2 -doped carbon nanosheets (Ni_3S_2 -CSs) for hydrogenolysis of lignin to aromatics.



Fig. 1 (a-i) SEM images of (a) the Ni₃S₂-CSs precursor, (b) Ni₃S₂-CSs-0.700, (c) Ni₃S₂-CSs-0.2-700, (d) Ni₃S₂-CSs-0.4-700, (e) Ni₃S₂-CSs-0.6-700, (f) Ni₃S₂-CSs-0.8-700, (g) Ni₃S₂-CSs-0.4-600, (h) Ni₃S₂-CSs-0.4-800 and (i) Ni₃S₂-CSs-0.4-900; (j) XRD patterns of Ni₃S₂-CSs-0.700, Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.4-900; (l) Raman spectra of Ni₃S₂-CSs-0.4-600, Ni₃S₂-CSs-0.4-800 and Ni₃S₂-CSs-0.4-800.

the preparation of the $\rm Ni_3S_2\text{-}CS$ sample, suggesting the excellent sustainability of our strategy.

2.4 Catalyst and product characterization

Powder X-ray diffraction (XRD) patterns of the catalysts were performed using a Bruker D8 Advance X-ray powder diffractometer using Ni filtered Cu K α radiation (λ = 1.5406 Å) with a scan speed of 2° min⁻¹ and a scan range of 10-80° at 30 kV and 15 mA. Scanning electron microscopy (SEM) was studied using a TESCAN-VEGA3 instrument. Transmission electron microscopy (TEM) images were collected using a TEM Tecnai G2 20 system. Raman spectra were recorded at room temperature using a Renishaw InVia micro-Raman spectrometer under laser excitation at 532 nm. The reducibility and acidity of catalysts were determined by H2-TPR and NH3-TPD on a Micromeritics AutoChem 2920 instrument. The X-Ray photoelectron spectroscopy (XPS) was examined using an ESCALAB-250 spectrometer (Thermo-VG Scientific, USA) with an Al K α (1486.6 eV) irradiation source. The conversion of the model compounds and the yields of the target products were detected by Gas Chromatography Mass Spectrometry (GC/MS, Agilent 7890A). GC/MS analysis was conducted on an Agilent 7890A system to study the chemicals in bio-oil, and GC/MS conditions were listed as follows: column, a capillary (60 m × 0.25 mm i.d.) coated with 0.25 m film of 5% phenyl methyl siloxane; carrier gas, high-purity helium; flow rate, 1.0 ml min^{-1} ; inlet mode and temperature, pulsed splitless at 190 °C; and the column temperature set at 60 °C and held for 2 min for injection, then programmed at 5 °C min⁻¹ to 145 °C and held for 25 min at the temperature of 145 °C, then at 5 °C min⁻¹ to 200 °C, and finally, at 20 °C min⁻¹ to 280 °C and held for 3 min at the temperature of 280 °C.

3. Results and discussion

3.1 Catalyst characterization

The scanning electron microscopy (SEM) images showed that the morphology of the 2D Ni₃S₂-CSs precursor consists of 2D nanosheets with a smooth surface (as shown in Fig. 1a). Subsequently, the 2D Ni₃S₂-CS precursor was calcined under a N₂ atmosphere and washed with ethanol three times to obtain the Ni₃S₂-CS catalyst with no apparent change in the morphology and crystalline form. The accurate thickness of 2D Ni₃S₂-CSs could be figured out in Fig. 1a, which was around 30 nm. When no nickel nitrate hexahydrate was added during the preparation of the Ni₃S₂-CSs-0-700 catalyst, 2D nanosheets with a smooth surface were obtained as in Fig. 1b. With an increase in the loading amount of nickel nitrate hexahydrate, the particle size of Ni₃S₂-CSs-X-700 samples increased and the phenomenon of agglomeration of metal particles appeared (Fig. 1b-1f). Fig. 1d shows that Ni₃S₂ particles displayed outside the activated carbon uniformly in the Ni₃S₂-CSs-0.4-700 catalyst. It was well known that the calcination temperature had a strong influence on the physicochemical properties of the final products, including the morphology, the components, and the particle size.³⁷ The morphologies of the series of Ni₃S₂-CSs-0.4 obtained at different temperatures are shown in Fig. 1d and 1g-1h. It could be concluded that the Ni₃S₂-CSs-0.4-700 catalyst possessed an excellent nanosheet structure calcined at 700 °C, and most Ni₃S₂ particles displayed outside the activated carbon uniformly. With an increase in temperature, the lamellar nanostructures of Ni₃S₂-CSs samples were destroyed. It could probably lead to poor catalytic activity than Ni₃S₂-CSs-0.4-700. Fig. 1i shows that Ni₃S₂-CSs-0.4-800 had an irregular structure at the micrometer

scale. Hence, the calcination temperature played a significant role in the morphology and structure of Ni₃S₂-CSs-0.4 samples.

The low peak intensities of the XRD patterns of Ni₃S₂-CSs-0-700 and Ni₃S₂-CSs-0.2-700 (Fig. 1j) implied weak crystallinity, resulting from a low loading amount of nickel nitrate hexahydrate. The XRD patterns of Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.6-700 and Ni₃S₂-CSs-0.8-700 exhibited diffraction peaks with 2θ values of 31.104°, 38.271°, 44.330°, 49.733° and 55.161°, which were indexed to the (110), (021), (202), (113) and (122) planes of Ni₃S₂ (Heazlewoodite, JCPDS No. 44-1418, a = b = 5.745 Å, c= 7.135 Å), respectively.³⁸ With an increase in the loading amount of nickel nitrate hexahydrate in the Ni₃S₂-CSs-0.8-700 catalyst, the diffraction peaks with the 2θ values of 44.401°, 51.846° and 76.370° were observed, which were indexed to the (200) and (220) planes of Ni (JCPDS No. 04-0850, a = b = c =3.524 Å), respectively. It was probably owing to the reduction of partial Ni₃S₂ to metallic nickel by activated carbon at a higher temperature.³⁹ In addition, XRD patterns of Ni₃S₂-CSs-0.4 calcined at different temperatures are shown in Fig. 1k. The low peak intensities of the XRD pattern of Ni₃S₂-CSs-0.4-600 implied weak crystallinity, indicating that the Ni₃S₂-CSs-0.4-600 catalyst was metastable. The metastable state may lead to instability during the use of the catalyst, which resulted in low conversion of 2-phenoxy-1-phenylethan-1-ol in Table 1. Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.4-800 and Ni₃S₂-CSs-0.4-900 all exhibited good crystallinity, indicating that these catalysts were stable.

Fig. 1l shows the Raman spectroscopy results of the Ni_3S_2 -CSs-0.4 catalyst at different calcination temperatures. All

samples showed the characteristic carbon peaks located at 1350 and 1570 cm⁻¹, which corresponded to the D and G bands, respectively. The G band could be utilized to analyze the degree of graphitization, while the D band was associated with partial disorder or defects of the graphitic domains. Herein, the intensity ratio of D and G bands (I_D/I_G) could be determined to evaluate the number of defects or the graphitization degree of carbon in composites.40 The D/G peak intensity ratio (I_D/I_G) was known to be an indicator of graphitization, where a smaller $I_{\rm D}/I_{\rm G}$ ratio indicated higher graphitization. Moreover, it could be clearly seen that the I_D/I_G values followed the order: Ni₃S₂-CSs-0.4-900 > Ni₃S₂-CSs-0.4-800 > Ni₃S₂-CSs- $0.4-700 > Ni_3S_2$ -CSs-0.4-600, indicating the ordered structure of carbon atoms and improved graphitization at a lower calcination temperature. The results were similar to those of a previous report. For example, Shuang *et al.* reported that the $I_{\rm D}/I_{\rm G}$ value of NiSx@C-800 was 1.045, while the $I_{\rm D}/I_{\rm G}$ value of NiS_x@C-600 was 0.838.³⁷

Based on the above characterization, it could be concluded that Ni_3S_2 -CSs-0.4-700 possessed a nano-size structure with high crystallinity and uniform dispersion. These favorable factors were conducive to the efficiency of the hydrotreatment process. The detailed morphology, component and other properties of Ni_3S_2 -CSs-0.4-700 were discussed below.

The Ni₃S₂-CSs-0.4-700 catalyst possessed a well-defined and robust 2D nanosheet structure (Fig. 2a and 2b). The inset in the transmission electron microscopy (TEM) image (Fig. 2b) indicated that the size distribution of Ni₃S₂ nanoparticles was uniform, and the average size is around 22.5 nm based on stat-

Table 1	Cleavage of β-O-4 lignin n	nodel compound	ds with different catalysts	3					
	$ \underbrace{Catalyst}_{iPrOH, 2 MPa N_2} + \underbrace{OH}_{iPrOH, 2 MPa N_2} + \underbrace{OH}_{iPrOH$								
	1		2	3	4	5	6		
					Yield ^b	(%)			
Entry	Cat.	Solvent	Temp. (°C)/ T (h)	$\operatorname{Conv.}^{b}(\%)$	2	3	4	5	6
1	None	iPrOH	260/4	0	0	0	0	0	0
2	С	iPrOH	260/4	0	0	0	0	0	0
3	Ni/AC	iPrOH	260/4	70	16	44	42	0	0
4	Ni/CNT	iPrOH	260/4	66	12	48	47	0	0
5	Ni ₃ S ₂ -CSs-0-700	iPrOH	260/4	0	0	0	0	0	0
6	Ni ₃ S ₂ -CSs-0.2-700	iPrOH	260/4	87	27	60	59	0	0
7	Ni ₃ S ₂ -CSs-0.4-700	iPrOH	260/4	100	9	92	86	0	5
8	Ni ₃ S ₂ -CSs-0.6-700	iPrOH	260/4	100	10	93	81	0	9
9	Ni ₃ S ₂ -CSs-0.8-700	iPrOH	260/4	100	9	92	80	0	10
10	Ni ₃ S ₂ -CSs-0.4-600	iPrOH	260/4	92	10	80	78	0	2
11	Ni ₃ S ₂ -CSs-0.4-800	iPrOH	260/4	90	18	70	66	0	1
12	Ni ₃ S ₂ -CSs-0.4-900	iPrOH	260/4	86	20	63	60	0	3
13 ^c	Ni ₃ S ₂ -CSs-0.4-700	iPrOH	260/4	100	22	77	76	0	0
14^d	Ni ₃ S ₂ -CSs-0.4-700	iPrOH	260/4	100	8	92	88	0	5
15^e	NiS-C-0.4-700	iPrOH	260/4	72	10	62	61	0	0

^{*a*} Reaction conditions: **1** (100 mg), Cat. (20 mg), iPrOH (10 mL), 2.0 MPa N₂, 260 °C, 4 h. ^{*b*} Conversion and yields were determined by GC/MS with *n*-dodecane as the internal standard. ^{*c*} The reaction was carried out with 10 mg of catalyst. ^{*d*} The reaction was carried out with 30 mg of catalyst. ^{*e*} The reaction was carried out with the NiS-C-0.4-700 catalyst prepared in two steps (impregnation followed by vulcanization).



Fig. 2 (a) SEM images of Ni_3S_2 -CSs-0.4-700, (b and c) TEM images of Ni_3S_2 -CSs-0.4-700, (insert of b) size distribution, (d) HRTEM image, (e) SAED image, (f) EDS spectrum of Ni_3S_2 -CSs-0.4-700, and (g–j) elemental mapping of Ni_3S_2 -CSs-0.4-700.

istics. The nanoparticles were uniformly embedded in the Ni₃S₂-doped carbon nanosheets (Fig. 2c). In addition, the lattice spacings of 0.234 nm and 0.237 nm match with those of the (-111) and (111) lattice planes of Ni₃S₂, respectively (shown in Fig. 2d). The selected area electron diffraction (SAED) image showed five diffraction rings (Fig. 2e). From inside to outside, these rings corresponded to the (110), (030), (022), (011), and (121) planes of Ni_3S_2 , respectively. The results were consistent with the XRD analysis. The EDS spectrum revealed that the sample contains the elements Ni, S, C and O as shown in Fig. 2e. The element O is attributed to the exposure to air. The C and S originated from the carbonization process of lignosulfonate, and the detected Ni components originated from the external addition of nickel nitrate in the preparation of the catalyst. As shown in the inset diagram of Fig. 3f, the Ni:S molar ratio determined by EDS analysis is close to 1.5:1, which is very approximate to the theoretical value of Ni₃S₂. The phenomenon was similar to the previous literature.⁴¹ In addition, the Ni:S molar ratio determined by ICP analysis is also close to 1.5:1 for Ni₃S₂-CSs-0.2-700, Ni₃S₂-CSs-0.4-700 and Ni₃S₂-CSs-0.6-700 (Table S1⁺). It was surprising to find that the Ni:S molar ratio of Ni₃S₂-CSs-0.8-700 was around 3:1. This corresponds to the XRD result that the (200) and (220) planes of Ni (JCPDS No. 04-0850, *a* = *b* = *c* = 3.524 Å) were observed. The elemental mapping results (Fig. 2g-j) of NiS_x@C-600 suggested that nickel and sulfur were well dispersed in the carbon nanosheets with distinct morphology of the nanoparticles.

Hydrogen temperature-programmed reduction $(H_2$ -TPR) characterization results of various catalysts are presented in Fig. 3a and 3b, which were used to reveal the redox behavior and the reaction activity of the Ni₃S₂-CSs-0.4-700 catalyst in the hydrogenolysis of lignin model compounds. Ni₃S₂-CS samples all displayed a broad hydrogen consumption peak over 329 °C, indicating that Ni₃S₂ on the carbon nanosheet support was difficult to be reduced at the reaction temperature of 260 °C, and Ni species thus was mainly presented as a mixture of high valence nickel oxides. This phenomenon corresponds to the result of XPS in Fig. 4 that only Ni oxide was detected. Therefore, Ni oxide (Ni₃S₂) species was likely in charge of hydrogenolysis in the transformation process of lignin model compounds. Comparing different Ni₃S₂-CSs-X-700 samples with different loading amounts, the H₂ consumption peak shifted to a lower temperature with an increase of the Ni amount from 0.4 g to 0.8 g, which indicated that a low loading amount of Ni was in favor of decreasing the reduction temperature, and consequently, it was a benefit for the hydrogenolysis process. However, the Ni₃S₂-CSs-0.2-700 catalyst showed a broad hydrogen consumption peak over 355 °C, suggesting poor reduction. Comparing different Ni₃S₂-CSs-0.4-Y catalysts at different calcination temperatures, the H₂ consumption peak appeared at a high temperature when Ni₃S₂-CSs-0.4-Y samples were calcined at 600 °C, 800 °C and 900 °C. 700 °C was in favor of the decrease in the reduction temperature, providing direct evidence that the Ni₃S₂-CSs-0.4-700 sample may have a positive effect on catalytic activity. To support the above viewpoint, Ni₃S₂-CSs catalysts with different Ni loading amounts and



Fig. 3 (a) H_2 -TPR profiles of Ni_3S_2 -CSs-X-700 with different loading amounts; (b) H_2 -TPR profiles of Ni_3S_2 -CSs-0.4-Y at different temperatures; (c) acid content of Ni_3S_2 -CSs-X-700 with different loading amounts; (d) acid content of Ni_3S_2 -CSs-0.4-Y at different temperatures.



Fig. 4 XPS spectra and fitted curves of (a) survey, (b) C1s, (c) S2p, and (d) Ni2p of the Ni₃S₂-CSs-0.4-700 catalyst.

at different calcination temperatures were used for the conversion of 2-phenoxy-1-phenylethan-1-ol. The results in Table 1 show that the yield of ethylbenzene and phenol achieved an excellent result when Ni_3S_2 -CSs-0.4-700 was employed in the hydrogenolysis process (Table 1, entry 7). In general, Ni oxide (Ni_3S_2) could play an important role in the hydrogenolysis process. In addition, the acidity of Ni_3S_2 -CSs-*X*-*Y* samples was

investigated by NH₃-TPD in Fig. 3c and 3d. It revealed that the acid amount increased with an increase of the nickel nitrate hexahydrate content (from 0 to 0.8 g) in Ni₃S₂-CSs-X-700 samples, whilst variation of calcined temperatures had little effect on the acid density according to the results of Ni₃S₂-CSs-0.4-600, Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.4-800 and Ni₃S₂-CSs-0.4-900 catalysts in Fig. 3d.

X-ray photoelectron spectroscopy was carried out to determine the chemical composition of the Ni₃S₂-CSs-0.4-700 catalyst. Fig. 4a depicts the XPS survey spectra of Ni₃S₂-CSs-0.4-700, proving the presence of C, O, S and Ni in the nanocomposite. It also indicated that the amounts of Ni and S were relatively low. Fig. 4b-4d show the corresponding high-resolution spectra of the C1s, S2p and Ni2p orbitals. The C1s spectra (Fig. 4b) showed three distinct peaks at 284.70 eV, 286.05 eV and 288.05 eV corresponding to C-C, C-S, and O=C, respectively.42 In S2p spectra (Fig. 4c), the peaks at 162.13 eV and 163.80 eV were attributed to Ni-S in Ni₃S₂-CSs-0.4-700. The S2p peaks at 165.20 eV and 167.25 eV shown in Fig. 4c were attributed to C-S in Ni₃S₂-CSs-0.4-700.³⁸ The main peaks of the high-resolution XPS spectrum of Ni2p (Fig. 4d) located at 855.10 eV and 857.56 eV were indexed to Ni2p3/2, whereas the peaks at 873.53 eV and 874.61 eV were indexed to Ni 2p1/2, which all corresponded to Ni oxide. The other peaks were satellite peaks.43-45 The XPS results demonstrated the successful formation of Ni₃S₂-doped carbon nanosheets.

3.2 Optimization of the reaction conditions

3.2.1 Effect of different catalysts. A series of heterogeneous Ni_3S_2 doped carbon nanosheet catalysts composed of different metal contents and calcined at different temperatures were prepared by wetness impregnation of metal precursors (nickel nitrate hexahydrate), template (boric acid) and carbon source (sodium lignosulfonate) followed by thermal treatment using N_2 . In our previous reports, ^{39,46–49} lignin model compounds were used to assess the activity of various catalysts.

Above all, a blank experiment without any catalysts was carried out to find that it failed to convert 2-phenoxy-1-phenylethan-1-ol to ethylbenzene and phenol (Table 1, entry 1). Moreover, solo support carbon (calcined sodium lignosulfonate) as a catalyst exhibited very poor activity in the conversion of 2-phenoxy-1-phenylethan-1-ol, providing yields of ethylbenzene and phenol less than 1% (Table 1, entry 2). In comparison, Ni/AC and Ni/CNT prepared by the traditional impregnation method^{39,49} led to an obvious increase in catalytic activity, affording ethylbenzene and phenol at 44%, 42% and 48%, 47% respectively (Table 1, entries 3 and 4). It was probably due to the possibility that Ni species could work as a catalytic center for C-O bond cleavage.46-49 Furthermore, conversion of 2-phenoxy-1-phenylethan-1-ol using different Ni₃S₂-CSs-X-700 samples (X: represents the mass of nickel nitrate hexahydrate added) are compared and presented in Table 1. It could be clearly seen that Ni₃S₂-CSs-0-700 achieved poor conversion and yields of the corresponding products (Table 1, entry 5), and Ni₃S₂-CSs-0.2-700, Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.6-700 and Ni₃S₂-CSs-0.8-700 provided higher catalytic activity. For Ni₃S₂-CSs-0.2-700 catalysts, incomplete conversion (87%), 60% yield of ethylbenzene and 59% yield of phenol were achieved, respectively. In addition, 27% yield of phenethoxybenzene as the intermediate was detected (Table 1, entry 6). For the latter three catalysts, complete conversion was achieved and a high yield of bond breaking products such as ethylbenzene (92%, 93%, and 92% yields over Ni₃S₂-CSs-0.4-700, Ni₃S₂-

CSs-0.6-700 and Ni₃S₂-CSs-0.8-700, respectively) and phenol (86%, 81%, and 80% yields over Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.6-700 and Ni₃S₂-CSs-0.8-700, respectively) were formed as main products. However, a small amount of cyclohexanol (5%, 9%, and 10% yields over Ni₃S₂-CSs-0.4-700, Ni₃S₂-CSs-0.6-700 and Ni₃S₂-CSs-0.8-700, respectively) was detected (Table 1, entries 7, 8 and 9). Based on the results above, we could draw a conclusion that an increase in the amount of Ni in our Ni₃S₂-CSs catalytic system led to a positive effect on the hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol: (1) an increase in the conversion and yields of the corresponding aromatic products, (2) further hydrogenation of phenol to cyclohexanol, and (3) better stability of ethylbenzene than phenol. For the Ni₃S₂-CSs-0.4-700 catalyst exhibited a good dispersion on the surface of the carbon nanosheets and in close contact with Ni₃S from the SEM results in Fig. 1. We used Ni₃S₂-CSs-0.4-Y (Y: represents the calcination temperature) as the catalyst in the subsequent optimization for hydrogenolysis of 2-phenoxy-1-phenylethan-1ol.

As for different calcination temperatures from 600 °C to 900 °C with the same reaction conditions (Table 1, entries 10–12), Ni₃S₂-CSs-0.4-700 performed the best catalytic performance regarding conversion and ethylbenzene and phenol yield. Further increasing the calcination temperature to 800 and 900, the conversion of 2-phenoxy-1-phenylethan-1-ol slightly decreased to 90% and 86% (Table 1, entries 11–12). Although Ni₃S₂-CSs-0.4-800 and Ni₃S₂-CSs-0.4-900 have a larger content of nickel, their lower catalytic activity could be owing to their large particle size, as metal nanoparticles with smaller sizes have been generally regarded to provide more active sites for the hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol.

Encouraged by the above promising result, the effect of the Ni₃S₂-CSs-0.4-700 amount (10 mg, 20 mg and 30 mg) was then explored. It could be seen that although 100% conversion was achieved, it failed to transform 2-phenoxy-1-phenylethan-1-ol into ethylbenzene and phenol completely, and 22% of phenethoxybenzene was detected, while 10 mg of the Ni₃S₂-CSs-0.4-700 catalyst was employed in the catalytic system. It was probably due to the low amount of catalyst leading to weak catalytic activity. Exceptionally, high yield of ethylbenzene and phenol (92% and 88%, respectively) while 30 mg of the Ni₃S₂-CSs-0.4-700 catalyst was employed in the catalytic system. Considering the concept of cost saving, 20 mg of the Ni₃S₂-CSs-0.4-700 catalyst was an ideal choice in the following experiments. In the end, the NiS-C-0.4-700 catalyst prepared by two steps (impregnation followed by vulcanization) was employed in the catalytic system, and moderate conversion (72%) and yields (62% and 61% for ethylbenzene and phenol) were achieved, which was slightly weaker than the Ni₃S₂-CSs-0.4-700 catalyst. Hence, the Ni₃S₂-CSs-0.4-700 catalyst stood out as an excellent catalyst in the cleavage of 2-phenoxy-1-phenylethan-1ol to obtain the corresponding aromatics.

3.2.2 Effect of N_2 pressure, reaction time, reaction temperature and solvent. The effect of the initial N_2 pressure, reaction time, reaction temperature and solvent on the conversion of 2-phenoxy-1-phenylethan-1-ol and selectivity toward ethyl-

benzene and phenol was investigated over the optimal Ni_3S_2 -CSs-0.4-700 catalyst, and the results are shown in Fig. 5a–f, respectively.

The influence of N₂ pressure on the conversion of 2-phenoxy-1-phenylethan-1-ol and selectivity to obtain ethylbenzene and phenol was studied by varying the N₂ pressure from 1.0 MPa to 3.0 MPa (Fig. 5a). The cleavage of 2-phenoxy-1-phenylethan-1-ol to ethylbenzene and phenol, and further hydrogenation of phenol to cyclohexanol was highly influenced by N2 pressure. The production of ethylbenzene and phenol was found to increase significantly with increasing N₂ pressure from 0.5 to 2.0 MPa. However, a further increase of pressure from 1.5 to 2.5 MPa led to a slight decrease in the amount of phenol observed. A slight decrease in the amount of phenol observed at a higher N₂ pressure (2.5 MPa) was most likely due to the phenol undergoing hydrogenation (where about 9% yield of cyclohexanol was observed) and the phenomenon was similar in our previous research studies.^{39,47} Zhou et al. found that the conversion rate of ethylbenzene to ethylcyclohexane was slightly lower than that of phenol to cyclohexanol, indicating that ethylbenzene was more stable than phenol.⁴⁶ Jiang et al. also discovered a similar phenomenon that phenol was gradually hydrogenated into cyclohexanol while ethylbenzene increased during the reaction process.⁵⁰ The result in our Ni₃S₂-CSs-0.4-700 catalytic system was consistent with the previous studies.

The influence of reaction time on product distribution over the Ni_3S_2 -CSs-0.4-700 catalyst was studied and the results are presented in Fig. 5b. The selectivity for ethylbenzene and phenol improved significantly upon increasing the reaction time from 1 h to 4 h with a maximum ethylbenzene and phenol yield occurring after 4 h (92% and 86%, respectively). Nearly 40% yield of phenethoxybenzene was detected an hour after the reaction, indicating that the low ethylbenzene and phenol production at shorter reaction times was due to a large amount of conversion of 2-phenoxy-1-phenylethan-1-ol to phenethoxybenzene as the intermediate. Zhou et al. also reported that phenethoxybenzene was the main intermediate in the conversion of 2-phenoxy-1-phenylethan-1-ol to cycloalkanes under similar reaction conditions (240 °C, 2.0 MPa H₂ and 4.0 h).⁴⁶ As could be seen in Fig. 5b, increasing the reaction time to 5.0 hours led to a slight decrease in phenol yield which was most likely due to the hydrogenation of phenol to cyclohexanol, which again confirmed that ethylbenzene was more stable than phenol. Hence, 4 h was employed as the optimal reaction time in the subsequent optimization of the catalytic reaction.

The effect of temperature was investigated in the range of 200 °C to 280 °C using the Ni₃S₂-CSs-0.4-700 catalyst in 2.0 MPa N₂ for 4 h, and the results of these tests are presented in Fig. 5c. The conversion of 2-phenoxy-1-phenylethan-1-ol increased gradually with an increase of temperature from 200 °C to 280 °C. The yield of ethylbenzene and phenol was however found to vary significantly with differing temperatures. The highest ethylbenzene and phenol yields (92% and 86%) were obtained at 260 °C and the lowest yields were obtained at 200 °C (less than 5%). At temperatures higher than 260 °C, the phenol yield was found to decrease where a slight decrease in yield was obtained at 280 °C (Fig. 5c). The lower phenol yields obtained at 280 °C (compared to the yield at 150 °C) were most likely due to the hydrogenation of phenol to cyclohexanol occurring at higher temperatures. Chen *et al.*



Fig. 5 Hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol over the Ni₃S₂-CSs-0.4-700 catalyst: (a) effect of N₂ pressure, reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 4 h, 260 °C and 10 mL iPrOH. (b) effect of reaction time, reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 260 °C and 10 mL of iPrOH. (c) effect of reaction temperature, reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 260 °C and 10 mL of iPrOH. (c) effect of reaction temperature, reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 4 h and 10 mL of iPrOH. (d) and effect of solvents, reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 4 h and 260 °C.

reported the high yield of cyclohexanol (nearly 100%) at elevated temperature (220 °C) after 4 h of reaction time over the Ni/CNT catalyst, whereas in the lower temperature (160 °C) the yield was quite poor (around 15%) which suggested that a higher temperature was favorable for the hydrogenation of phenol to cyclohexanol.³⁹

Solvent also played a key role in the cleavage of 2-phenoxy-1-phenylethan-1-ol. Thus, the following catalytic reaction was investigated under the following conditions: pressure: 2.0 MPa N₂, time: 4 h, temperature: 260 °C, and 20 mg of the Ni₃S₂-CSs-0.4-700 catalyst. Compared with iPrOH, the transfer hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol in primary alcohols such as methanol and ethanol produced much low conversion and yields of ethylbenzene and phenol (Fig. 5d), due to the difficulty of eliminating β-hydrides from primary alcohols on the surface of the catalysts,^{50,51} and thus resulted in the fact that the secondary alcohol isopropanol could give higher activity than those primary alcohols.⁵² When iPrOH was used as a solvent in the catalytic process, 92% and 86% yield of ethylbenzene and phenol were obtained. Methanol and ethanol were reported to be beneficial for reducing the remaining solid residue after the depolymerization reaction because methanol and ethanol have the high dissolution capability of lignin.53 In addition, the use of ethanol and iPrOH in the catalytic reaction was sustainable since both of them can be produced from biomass. Therefore, a mixed solvent was used in the Ni₃S₂-CSs-0.4-700 catalytic system. However, the yield of ethylbenzene and phenol had a slight decrease than iPrOH used in the Ni₃S₂-CSs-0.4-700 catalytic system. In addition, ethylene glycol and formic acid were also used as a solvent in the catalytic system. Poor conversion was obtained. Thus, iPrOH was thus selected as the optimal solvent (Fig. 5d). Through comprehensive screening of the reaction conditions, the optimal reaction conditions were then established and the appropriate reaction pressure, time, temperature and solvent were 2.0 MPa N₂, 4 h, 260 °C, and 10 mL of iPrOH.

3.2.3 Hydrogenolysis of various lignin model compounds. To generalize the protocol, the Ni₃S₂-CSs-0.4-700 catalyst was employed to cleave various ether bonds containing β -O-4, α-O-4 and 4-O-5, which accounts for 5%-10%, 15%-30% and 30%-50% of all ether bonds, respectively.47 As indicated in Table 2, Ni₃S₂-CSs-0.4-700 exhibited promising catalytic activity and yield for model compounds containing β -O-4 bonds with a C_{α} -OH unit (Table 2, entries 1–6). It was interesting to find that more methoxy groups substituted on the O-terminus aryl ring resulted in a negative effect on the transformation of β-O-4 model compounds and yields of the corresponding products. For example, yields of 2,6-dimethoxyphenol, 2-methoxyphenol and phenol were 83%, 80% and 78%, which showed a downward trend (Table 2, entries 4-6). High conversion and yields of ethylbenzene and phenol were obtained for 2-phenoxy-1-phenylethan-1-one (Table 2, entry 7). It was probably owing to the possibility that the ketone substituted on the C_{α} activated β -O-4 ether bond. However, with substrates that do not contain these units at the C_{α} position, conversion and yields decreased, typically around 88% (Table 2, entry 8). It is

Table 2 Cleavage of the $\beta\text{-}O\text{-}4$ ether bond over the $Ni_3S_2\text{-}CSs\text{-}0.4\text{-}700$ catalyst^a

R ₁	R_2 R_3 R_4 $\frac{2}{4}$	i ₃ S ₂ -CSs-0.4-700 Mpa N ₂ , 260 ℃ h, 10 ml iPOH	+ R4	ОН
Entry	Substrate	Conversion ^{b} (%)	$\operatorname{Yield}^{b}(\%)$	
1	OH OF	100	07 07	OH e
2	OH OMe	98		OMe OH OH
3	OH OMe MeO	91	84	OMe OH OH OH OMe
4	Meo	100	MeO 89	OMe OH 83
5	MeO OH OMe	90	MeO 82	0H 80
6	Meo Meo	88	MeO 81	OMe OH OMe 78
7		100	98	96 OH
8		88		OH
9		80	86 MeO 42 MeO 42 MeO 34	85 OMe OH 72
10	Heo OH OH	88	MeO 45	OMe OH 74

^a Reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 260 °C and 10 mL of iPrOH. ^b Conversion and yields were determined by GC/MS with *n*-dodecane as the internal standard.

worth noting that β -O-4 model compounds with γ -OH, which represented the lignin typical realistic segment underwent C-O bond cleavage. Therefore, two more complicated dimeric model compounds 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)propane-1,3-diol and 2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propane-1,3-diol are also studied in Table 2. However, the optimal reaction conditions were not beneficial for the cleavage of the C-O bond. By increasing the temperature and prolonging the reaction time, 76% yield of ethylbenzene derivatives (42% 4-ethyl-1,2-dimethoxybenzene and 34% 1,2dimethoxy-4-propylbenzene) and 72% yield of 2-methoxyphenol were observed in Table 2 (entry 9). 2-(2-methoxyphenoxy)-1-(3-methoxyphenyl)propane-1,3-diol also could obtain the similar result (Table 2 entry 10). 77% yield of ethylbenzene derivatives (45%) 1-ethyl-4-methoxybenzene and 32% 1-methoxy-4-propylbenzene) and 74% yield of 2-methoxyphePaper nol were detected. It was probably due to the strong steric hindrance in these two model compounds, which usually hindered the β -O-4 ether cleavage. Based on all the above results, all these examples above demonstrated that the Ni₃S₂-CSs-0.4-700 catalyst exhibited perfect catalytic cleavage of various compounds containing β -O-4 ether bonds to generate the corresponding ethylbenzene and phenol derivatives, which could provide a novel route for the generation of aromatic hydro-

carbons and aromatic alcohols by catalytic hydrotreatment of

lignin dimeric model compounds. Inspired by the good performance in the hydrogenolysis of β -O-4 ether bonds, we next proceeded to explore a different range of α -O-4 ethers and 4-O-5 ether bonds at 260 °C under 2.0 MPa N₂, using Ni₃S₂-CSs-0.4-700 as a catalyst in iPrOH for 4 h. Among these ether bonds, the C-O bond dissociation energies were following the order: 4-O-5 $(315 \text{ kJ mol}^{-1}) > \beta$ -O-4 (296 kJ mol⁻¹) > α -O-4 (245 kJ mol⁻¹).⁴⁷ As shown in Table 3, good to remarkable yields were obtained for a variety of α -O-4 substrates (Table 3, entries 1-6). It was easy to find that the conversions of different α -O-4 model compounds were high enough (up to 100%), while the yields of toluene and phenol varied with each other. Substituent groups on the aromatic rings played a significant factor in this catalytic process. For instance, methyl benzyl ether without any substitution groups on the aromatic rings could obtain 100% conversation, 94% yield of toluene and 89% yield of phenol, respectively (Table 3, entry 1). Methoxy groups substituted at the para-position of the O-terminus aryl ring resulted in nearly 100% conversion and yielded 88% of toluene and 55% of 4-methoxyphenol (Table 3, entry 2). High conversion and yields were obtained with benzyloxy substitution at the para-position of the O-terminus aryl ring (Table 3, entry 3), which revealed that electron-donating groups substituted at the O-terminus aromatic ring obtained an excellent result of the cleavage of α -O-4 ethers. When the O-terminus aromatic ring was substituted with a hydroxyl group, a slight decrease in the conversion and yields of the corresponding products regardless of the position of the hydroxyl group on the O-terminus aromatic ring (ortho-, meta-, or para-position). As shown in Table 2, 4-(benzyloxy)phenol could yield 90% yield of toluene and 80% yield of phenol (Table 3, entry 6), while 2-(benzyloxy)phenol could yield 72% yield of toluene and 72% yield of phenol (Table 3, entry 4). It was probably due to the strong steric hindrance in 2-(benzyloxy)phenol, which usually hindered the α -O-4 ether cleavage in lignin. The above results indicated that the symmetrical structure with an electron donating group was beneficial for the cleavage of $\alpha\text{-}O\text{-}4$ ether bonds over the $Ni_3S_2\text{-}CSs\text{-}0.4\text{-}700$ catalyst in iPrOH.

When 4-O-5 model compounds were used as substrates in the reaction process, poor results were achieved compared to β -O-4 and α -O-4 model compounds. It was probably owing to the highest C–O bond dissociation energies than β -O-4 and α -O-4 ether bonds. As shown in Table 3, diphenyl ether could not be totally converted to yield benzene (68%) and phenol

R1		i ₃ S ₂ -CSs-0.4-700 Mpa N ₂ , 260 °C H, 10 ml iPOH	+ R211 OH
			n=1, 0
Entry	Substrate	Conversion ^{b} (%)	$\operatorname{Yield}^{b}(\%)$
α-0-4	~	100	
1		100	94% 89%
2	OMe	95	0H 88% MeO 85%
3	OBn	94	0H
4	ОООН	80	72% 72% OH
5	Сосон	83	HO OH 78% 76%
6	ОПОСТОН	95	90% HO 80%
4-O-5 7		70	68 62 OH
8		68	60 61
9	но	72 H	
10		52	50 43
11	() ⁰	15	0H 12

^a Reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 2.0 MPa N₂, 260 °C and 10 mL of iPrOH. ^b Conversion and yields were determined by GC/MS with *n*-dodecane as the internal standard.

(62%), respectively (Table 3, entry 7). When diphenyl ethers were substituted with methyl and hydroxyl groups at the paraposition, around 70% conversion of 4-O-5 model compounds was achieved and the yields of corresponding benzene and phenol derivates were moderate (Table 3, entries 8-9). In addition, only one side methyl substituted diphenyl ether was used in our reaction process. Poor conversion and yields (50% of benzene and 43% of *m*-cresol, respectively) were achieved, which also indicated that symmetrical structures with substituent groups were beneficial for the cleavage of 4-O-5 ethers over the Ni₃S₂-CSs-0.4-700 catalyst (Table 3, entry 10). The phenomenon was similar to the results of the cleavage of α -O-4 ether bonds. In addition, the Ni₃S₂-CSs-0.4-700 catalyst hardly converted anisole to phenol and the yield of phenol was 12%. In general, the Ni₃S₂-CSs-0.4-700 catalyst exhibited good catalytic cleavage of various compounds containing β -O-4, α -O-4 and 4-O-5 ether bonds to generate the corresponding aromatic hydrocarbons and aromatic alcohols, which could provide a novel route for the transformation of lignin model compounds.

Encouraged by the excellent result of catalytic hydrogenolysis of lignin model compounds, alkaline lignin was employed in our catalytic system. The changes in molecular weight between alkaline lignin and residual lignin were detected in order to study the relationship between depolymerization and repolymerization reactions. The results of weight-average molecular weight (M_w) , number-average molecular weight (M_n) and polydispersity index (PDI) of alkaline lignin and residual lignin after depolymerization under different reaction conditions are shown in Table S3.[†] It indicated that the molecular weight of all residual lignin samples from the reactions performed under different reaction conditions showed slight changes relative to the alkaline lignin (2092 g mol^{-1}). It was found that the molecular weight of residual lignin samples decreased from 2092 g mol⁻¹ to 1610 g mol⁻¹ at a high temperature and a longer reaction time. This could be explained on the basis that the effect of reaction temperature and reaction time on the catalytic depolymerization of alkaline lignin was to enhance the bond cleavage in the lignin structure leading to a decrease of the molecular weight. Therefore, it is worth looking forward to finding a modified Ni₃S₂-CSs-0.4-700 catalyst to improve the depolymerization, and the hydrogenolysis of real lignin is a key point in our further study.

3.3 Possible reaction pathway

It was of great significance to explore the cleavage of the lignin ether bond to obtain the corresponding aromatics. The proposed pathway was started from a possible species of active hydrogen produced by iPrOH, followed by protonation of C_{α} -OH with an active hydrogen. Phenethoxybenzene was obtained as an intermediate after the dehydration process. The H then reacted with the O atom in phenethoxybenzene to produce phenol via the cleavage of the C-O ether bond. Subsequently, 2-phenylethan-1-ylium (C₆H₅-CH₂CH₂⁺) abstracted H⁻ from the $C\alpha$ -OH⁻ of iPrOH to afford ethylbenzene. Meanwhile, the produced acetone was released into the reaction system, which was detected by GC/MS. In general, the Ni₃S₂-CSs-0.4-700 catalyst was an extremely active catalyst for the reaction while preserving aromatic products. The time course of the product distribution was explored for the transfer hydrogenolysis of 2-phenoxy-1-phenylethan-1-ol over the Ni₃S₂-CSs-0.4-700 catalyst at 260 °C. 2-phenoxy-1-phenylethan-1-ol was completely consumed after 4 h in iPrOH. The slope of the conversion rate duirng 4 h was large, which suggested that high conversion of the β-O-4 model compound occurred due to a high concentration of 2-phenoxy-1-phenylethan-1-ol during this time period. In the early 1 h, ethylbenzene, phenol and phenethoxybenzene were the major intermediate products (Fig. S3[†]). With the extension of the reaction time, the yield of phenethoxybenzene first increased and then decreased, indicating that phenethoxybenzene was an important intermediate. In addition, ethylbenzene and phenol were major products which suggested the cleavage of the C-O bond of phenethoxyben-



Fig. 6 Proposed pathway for the catalytic hydrogenolysis of lignin model compounds over the Ni_3S_2 -CSs-0.4-700 catalyst.



Fig. 7 The recycling of the Ni₃S₂-CSs-0.4-700 catalyst. Reaction conditions: 20 mg of Ni₃S₂-CSs-0.4-700 catalyst, 4 h, 2.0 MPa N₂, 260 °C and 10 mL of iPrOH.

zene. This result was also consistent with our expected reaction process (Fig. 6).

3.4 Recycling experiments

The cycling experiment of the Ni₃S₂-CSs-0.4-700 catalyst was studied under the optimal reaction conditions, demonstrating that it could be repeatedly employed in the next five runs with only a slight decrease in the activity (the conversion of 2-phenoxy-1-phenylethan-1-ol decreased from 100% to 92% after five runs). Moreover, the yields of the corresponding ethylbenzene and phenol remained largely constant with only a slight decrease after five runs. However, the XPS surface content of the recycled Ni₃S₂-CSs-0.4-700 catalyst indicated that some Ni_3S_2 had leached from the surface of the carbon nanosheet (Table S1[†]), although the oxidation states appear to be unchanged (XPS spectra of the used Ni₃S₂-CSs-0.4-700 catalyst in Fig. S1[†]) and no obvious changes in the catalyst structure were detected in the XRD pattern (XRD pattern of the fresh and used Ni₃S₂-CSs-0.4-700 catalyst in Fig. S2[†]). In addition, the Ni₃S₂-CSs-0.4-700 catalyst was washed with iPrOH after each run. Therefore, the mechanical loss during the separation also led to the deactivation of the Ni₃S₂-CSs-0.4-700 catalyst (Fig. 7).

4. Conclusions

In this work, we first reported a facile yet sustainable approach for the production of Ni₃S₂-doped carbon nanosheets in onestep with a very thin thickness of 30 nm and excellent flexibility by assembling the biomass molecule in long-range order on a 2D hard template and subsequent annealing. Sodium lignosulfonate was used as the carbon and sulfur source because it was the reaction product of wood pulp with sulfur dichloride and sulfite, thus containing a large number of S elements. Boric acid was employed as a 2D template, which could be readily recycled for repeated use by simple evaporative crystallization from the waste liquid. In addition, it also could be applied in the cleavage of C-O bonds to obtain the corresponding aromatics under mild reaction conditions without external H₂ (260 °C, 2.0 MPa N₂, 4 h). A range of α-O-4, β-O-4 and 4-O-5 model compounds were explored under the optimal conditions, which achieved a pretty good result. The Ni₃S₂-CSs-0.4-700 catalyst showed good stability during the reaction, and no obvious change had been discovered after five cycles. Further studies will focus on the degradation of lignin and more complex model compounds over the Ni₃S₂-CSs-0.4-700 catalyst and the mechanism for C-O ether bond cleavage. In general, we use a novel approach with sodium lignosulfonate as a raw material to prepare catalysts for the cleavage of lignin model compounds. The starting materials are cheap and the reaction was fast, efficient, and environmentally friendly, consistent with the concept of green chemistry.

Conflicts of interest

The authors have no conflicts of interests.

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